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Performance Report :

THE ROLE OF SEMICONDUCTING MINERALS IN THE PREBIOTIC FIXATION OF NITROGEN AND CARBON

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Much of the work focused on the photoreduction of carbon dioxide by iron(II) sulfide particles. Typical experiments consisted of irradiation of commercially available iron(II) sulfide powders in water at pH 7-8. Irradiation was broad band light, pyrex filtered, from a medium pressure mercury are lamp. Preliminary results indicated the presence of trace organics in the solutions after irradiation. However, currently results seem to indicate that contamination of the commercial powder is the course of those organics. It has also been decided that future experiments should focus on colloidal suspensions of iron(II) sulfide.

Work also focused on the question of wether the Strecker synthesis can be carried out in the presence of iron(II). Typical experiments consisted of following the formation of glycine Iminodiacetic acid as a function of time in a reaction mixture consisting of; CN^{-1} (0.1M) , iron (II) (either Fe^{+2}, 0.1M, or FeS, 0.2 g/ml), formaldehyde (0.1M), and NO_2^-. In some cases iron (II), and nitrite were removed or ammonia was added as a control. Preliminary results showed that the Strecker synthesis is not poisoned by aqueous iron(II) or iron sulfide particles. Results also indicated the possibility of some catalytic effect in the Strecker synthesis.

During this period, a paper entitled "Experimental Results on the Prebiotic Fixation of Nitrogen Under a Neutral Atmosphere by Iron(II)" was presented at the First International Conference on Circumstellar Habitable Zones (See Abstract). A paper entitled "Prebiotic ammonia from reduction of nitrite by iron (II) on the early Earth" was published in Nature (see photocopy of first page).

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(Abstract From the First International Conference on Circumstellar Habitable Zones)

Experimental Results on the Prebiotic Fixation of Nitrogen Under a Neutral Atmosphere by Iron(II)

Theories for the origin and evolution of life depend on the availability of reduced or "fixed" nitrogen. In a strongly reducing atmosphere, amino acids essential to the chemical evolution of life can from by reactions between HCN, NH_3, and carbonyl compounds produced in spark discharges.[1] However, under neutral atmospheres NO, rather than HCN or NH_3 is produced atmospherically.[3] This raises the questions of; how ammonia can be formed under a neutral atmosphere, and what conditions are needed such formation to occur? One possibility is the reduction of nitrite, formed from the NO,[4] by aqueous Fe(II) such as was present on the early Earth.[1,5] We wish to describe experimental results showing that the reduction of nitrite and nitrate to ammonia by Fe(II) (equation 1), is plausible

$$6\, Fe^{+2} + 7\, H^{+} + NO_2^{-} \rightarrow 6\, Fe(III) + 2\, H_2O + NH_3 \qquad (1)$$

under prebiotic seawater conditions. Nitrite reduction follows an apparent rate law of the form Rate = $k\, [NO_2^{-}]\, [Fe]^{1.8}$ and is not significantly inhibited by many of the solutes found in the modern day ocean. The reaction is favored by temperatures ≥ 25 °C, but only proceeds at pH > 7.3.

1) *Earth's Earliest Biosphere*, J. William Schopf, Ed., Princeton NJ: Princeton University Press (1983), and references therein.

2) a) J. C. G. Walker, *Origins of Life*, **16**(1985)117-127; b) G. S. Mattioli and B. J. Wood, *Nature*, **322**(1986)626-628.

3) a) W. L. Chameides and J. C. G. Walker, *Origins of Life*, **11**(1981)291-302; b)Y. L. Yung and M. B. McElroy, *Science* **203**(1979)1002. b) J. F. Kasting, *Origins of Life*, **20**(1990)199.

4) R. L. Mancinelli and C. P. McKay, *Origins of Life*, **18**(1988)311-325.

5) J. C. G. Walker and P. Brimblecombe, *Precambrian. Res.*, **28**(1985)205-222.

Prebiotic ammonia from reduction of nitrite by iron (II) on the early Earth

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THEORIES for the origin of life require the availability of reduced (or 'fixed') nitrogen-containing compounds, in particular ammonia. In reducing atmospheres, such compounds are readily formed by electrical discharges[1,2], but geochemical evidence suggests that the early Earth had a non-reducing atmosphere[1,3–6], in which discharges would have instead produced NO (refs 7–10). This would have been converted into nitric and nitrous acids and delivered to the early oceans as acid rain[11]. It is known[12–15], however, that Fe(II) was present in the early oceans at much higher concentrations than are found today, and thus the oxidation of Fe(II) to Fe(III) provides a possible means for reducing nitrites and nitrates to ammonia. Here we explore this possibility in a series of experiments which mimic a broad range of prebiotic seawater conditions (the actual conditions on the early Earth remain poorly constrained). We find